Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

April 1, 2004 – June 30, 2004

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Cooperative Agreement No: DE-FC26-04NT41992

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DISCLAIMER

ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-04NT41992, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," during the time-period April 1, 2004 through June 30, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being cofunded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Energy, and Duke Energy. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months or longer at each of two sites to provide longer-term catalyst life data. Pilot-scale wet FGD tests will be conducted periodically at each site to confirm the ability to scrub the catalytically oxidized mercury at high efficiency. The pilot wet FGD system will also be used downstream of catalysts currently being tested as part of another cooperative agreement (DE-FC26-01NT41185). The catalyst pilot units to be used on project 41992 are currently in use on project 41185; pilot catalyst testing on project 41992 will commence after the catalyst tests for project 41185 are completed.

This is the second reporting period for the subject Cooperative Agreement. During this period, project efforts included completing the design and fabrication of the pilot wet FGD system, and laboratory testing to determine the activity of candidate catalysts at simulated Monticello Plant conditions. This Technical Progress Report describes the completion of the pilot wet FGD system and results of the laboratory tests completed to date.

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INTRODUCTION

This document is the quarterly Technical Progress Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," for the time-period April 1, 2004 through June 30, 2004. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion, and the use of a wet flue gas desulfurization (FGD) system downstream to remove the oxidized mercury at high efficiency. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory, EPRI, Great River Energy (GRE), TXU Energy, and Duke Energy. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone FGD systems. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale and in a commercial form, to provide engineering data for future full-scale designs. The pilot-scale tests will continue for approximately 14 months or longer at each of two sites, to provide longer-term catalyst life data. Pilot-scale wet FGD tests will be conducted periodically at each site to confirm the ability to scrub the catalytically oxidized mercury at high efficiency. The pilot wet FGD system will also be used downstream of catalysts currently being tested as part of another cooperative agreement (DE-FC26-01NT41185). The catalyst pilot units to be used on project 41992 are currently in use on project 41185; pilot catalyst testing on project 41992 will commence after the catalyst tests being conducted as part of project 41185 are completed.

Four utility team members are providing project host sites for testing. GRE is providing a test site at their Coal Creek Station (CCS), which fires North Dakota lignite. City Public Service of San Antonio (CPS) is providing a test site at their J.K. Spruce Plant, which fires Powder River Basin (PRB) subbituminous coal. Both CCS and Spruce are currently hosting mercury oxidation catalyst pilot tests as part of project 41185. They will also host pilot FGD tests downstream of the catalysts as part of the current, 41992 project.

For the current project, TXU will be hosting pilot catalyst tests and intermittent wet FGD pilot tests at their Monticello Station, which fires a Texas lignite/Power River Basin (PRB) coal blend. The TXU test program will commence after the current testing at CCS is completed the spring of 2004. Duke Energy will also host oxidation catalyst pilot and wet FGD pilot tests, at one of their sites firing a low-sulfur Eastern bituminous coal. The Duke Energy tests will commence after the current testing at Spruce is completed at the end of calendar year 2004.

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, April 1, 2004 through June 30, 2004, is the second technical progress report period for the project. Efforts over the current period included completing the design and fabrication of the pilot wet FGD system, and laboratory testing to determine the activity of candidate catalysts at simulated Monticello conditions.

One subcontract was issued during the current reporting period, to Skotz, Inc. of Austin, Texas, for fabrication of the pilot wet FGD equipment skid and associated items.

Problems Encountered

There were no significant problems encountered during the reporting period.

Plans for Next Reporting Period

During the next reporting period (July 1 through September 30, 2004), pilot-scale wet FGD tests will be conducted downstream of oxidation catalysts being operated at CCS as part of another DOE-funded project (DE-FC26-01NT41185), to determine how effectively the catalytically oxidized mercury will be scrubbed.

The catalyst pilot unit at CCS will be shut down after the wet FGD tests are completed, and that pilot unit will be shipped to Monticello, where plant staff will install it adjacent to the 3C induced draft (ID) fan on Unit 3. Catalyst testing should commence at the Monticello site by late September.

Also, once the pilot wet FGD tests are completed at CCS, the wet scrubber pilot will be shipped to Duke Energy's Marshall Station, where baseline (no mercury oxidation catalyst upstream) mercury removal tests will be conducted. These tests are scheduled to be conducted in August.

Prospects for Future Progress

During the next reporting period (October 1 through December 31, 2004), catalysts will be evaluated for elemental mercury oxidation activity at Monticello through routine (~monthly to bimonthly) evaluation trips. Intensive gas characterization efforts and initial wet FGD pilot testing should also occur during the quarter. Also during the quarter, pilot wet FGD tests will be conducted at CPS' Spruce Plant.

EXPERIMENTAL

The work being conducted as part of this project will use three different experimental apparatus types. One is an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated), the first of which is currently located at GRE's CCS Station in North Dakota. A second, nearly identical pilot unit is currently located at CPS' Spruce Plant. During the course of this project, these two pilot units will be relocated and installed at TXU Energy's Monticello Plant and at a Duke Energy plant, respectively.

Each pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports as part of the ongoing 41185 project[1,2,3,4]. The activity of these catalysts is determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report[5]. Periodically, the analyzer results are verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

The second experimental apparatus is a bench-scale test unit that is used to evaluate the activity of candidate catalyst samples under simulated flue gas conditions. The bench-scale catalyst oxidation test apparatus was previously described in quarterly technical progress reports for the 41185 project[3,4].

The third experimental apparatus is a pilot-scale wet FGD unit that is being designed and fabricated as part of the current, 41992 project, to allow the measurement of how effectively catalytically oxidized mercury can be scrubbed. The pilot unit was designed to treat the flue gas from one of four catalyst chambers on either of the mercury oxidation catalyst pilot units. The design basis and a simplified piping and instrumentation diagram (P&ID) for the pilot wet FGD system were included in the previous technical progress report for this project.[6]

The design and fabrication of the pilot unit was completed during the current quarter. Figure 1 shows the completed wet FGD pilot skid as installed at Great River Energy's Coal Creek Station in early July. The oxidation catalyst pilot is shown in the background, to the right of the pilot FGD in the photo, although it is difficult to make out any details of the oxidation catalyst skid because of the plywood structure that was erected around it for weather protection.

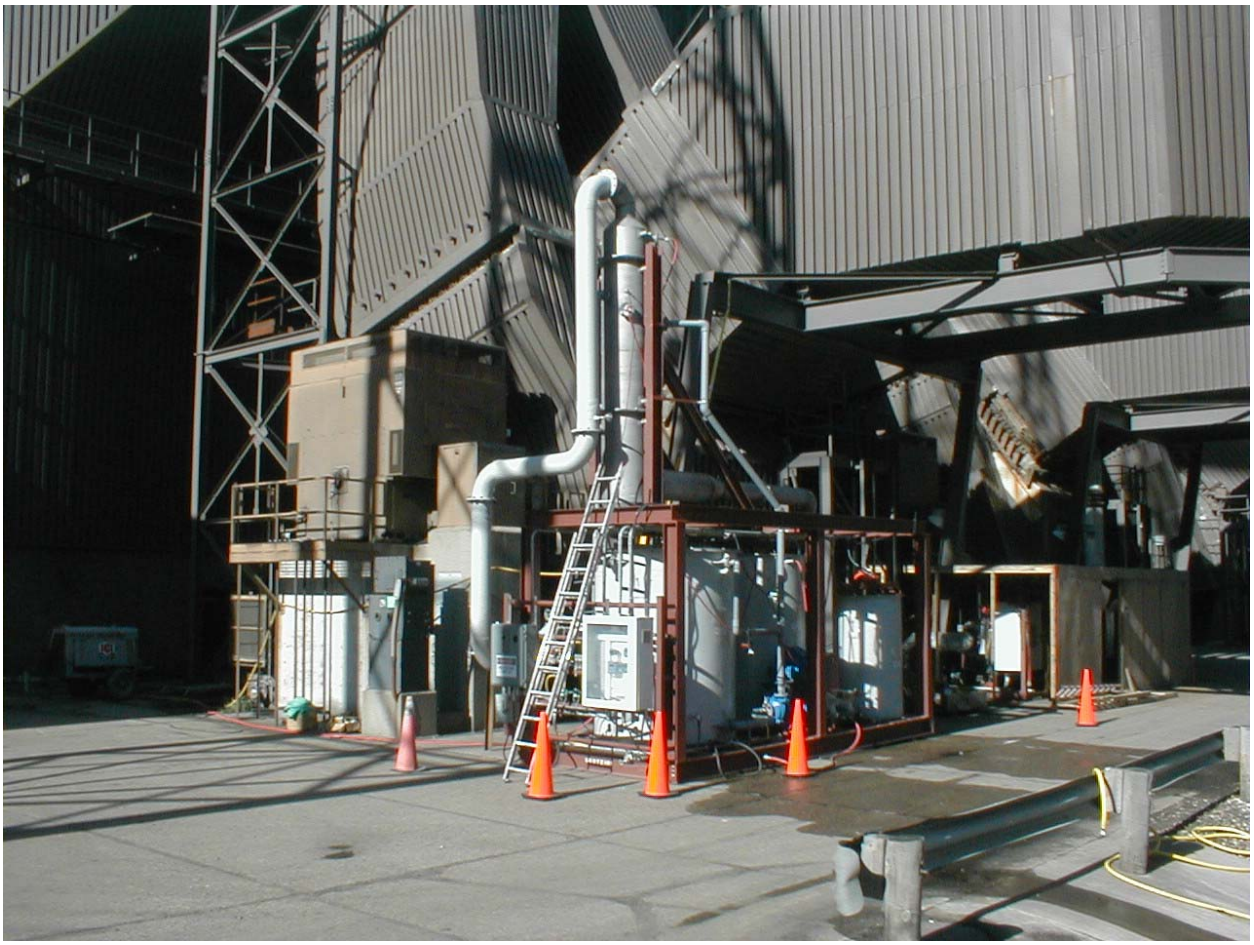

Figure 1. Pilot Wet FGD System Installed at Coal Creek Station

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period, April 1, 2004 through June 30, 2004. Results to date have been limited to laboratory activity screening of candidate catalyst materials for the upcoming pilot tests.

Laboratory Evaluation of Candidate Catalysts

Laboratory evaluation of candidate catalyst materials at simulated Monticello Station Unit 3 conditions continued. Four catalyst materials were tested during the quarter: two palladium catalysts (one from Sud-Chemie Prototech, that has previously supplied the Pd #1 catalyst tested at Coal Creek and Spruce, and one from an alternate supplier that does not wish to be identified); gold prepared by Sud-Chemie Prototech; and an SCR catalyst previously supplied by Argillon, who supplied the SCR catalysts tested at Coal Creek and Spruce. During the previous quarter, three additional catalyst materials were evaluated: an SCR catalyst from Mitsubishi Heavy Industries; a sample of Pd #1 prepared by Johnson Matthey, another supplier being considered for supply of the catalysts for Monticello; and a sample of the carbon-based (C #6) material from the 2002 production run to make the catalyst currently being tested at Coal Creek Station as part of project 41185. Thus, laboratory results are now available for seven candidate catalysts for the pilot testing at Monticello.

Table 1 shows the simulation gas species concentrations, and Table 2 shows the results of tests conducted through the end of June. All of the results shown are based on the use of "Tris" solutions (rather than with KCl solutions) in the Hg analyzer impinger train when measuring elemental mercury concentrations downstream of the catalysts. However, the catalyst outlet gas elemental mercury concentrations were measured twice, once with KCl and once with Tris impingers, and the results were typically similar.

Table 1. Target Simulation Gas Composition for Monticello Laboratory Tests

Species	Concentration
Hg^0	45-57 $\mu g/Nm^3$
SO_2	600 ppmv
HCl	1 ppmv
NO_X	400 ppmv
H_2O	15%
CO_2	12%
O_2	6%
N_2	Balance

Table 2. Laboratory Catalyst Activity Test Results, April Through June 2004

Catalyst	Core Length, in.	Cell Pitch, cpsi	No. of Cells in Core	Flow Rate, L/min	Area Velocity, sft/hr	Hg Concentration ($\mu g/Nm^3$)		Hg^0 Oxidation, %
						Inlet Total	Outlet Hg^0	
Prototech Pd #1	1.04	64	14	0.61	28	65.4	1.38	98
Prototech Pd #1	1.04	64	14	0.93	42	63.5	8.28	87
Prototech Pd #1	1.04	64	14	1.44	65	65.4	7.36	89
Prototech Au	0.94	64	14	0.61	30	64.4	0.00	100
Prototech Au	0.94	64	14	0.93	46	60.8	0.92	98
Prototech Au	0.94	64	14	1.44	72	63.1	4.14	93
Supplier #2 Pd #1	1.02	64	11	0.61	36	65.8	0.92	99
Supplier #2 Pd #1	1.02	64	11	0.93	54	64.4	5.06	92
Supplier #2 Pd #1	1.02	64	11	1.44	84	63.5	10.13	84
Argillon SCR	1.04	50	8	0.61	43	64.0	5.52	91
Argillon SCR	1.04	50	8	0.93	65	64.0	9.20	86
Argillon SCR	1.04	50	8	1.44	101	65.8	17.03	74

Figure 2 shows a plot of these data, with elemental mercury oxidation across the catalyst cores on the "Y" axis and the effective catalyst area velocity on the "X" axis. Also plotted are data from last quarter for the Johnson Matthey Pd #1 core, so the results for all three potential suppliers of Pd #1 can be visually compared. Note that the gold catalyst is the most active of the catalysts tested. Also note that the middle data point for the Prototech Pd #1 appears to be an outlier, as the oxidation should gradually drop with increasing area velocity, and the data at the middle area velocity should not show a lower oxidation percentage than the data at the highest area velocity. Of the three potential sources for Pd #1, the material from Supplier #2 appears to be the most active over the range of area velocity values tested, although not by a wide margin relative to the other suppliers.

Figure 3 shows the data from the catalyst tests conducted in the previous quarter, with the current Argillon SCR catalyst data added to the plot. This allows the data for the MHI and Argillon SCR catalysts to be directly compared. Based on these data, the MHI catalyst appears to be slightly more active than the Argillon catalyst for elemental mercury oxidation at the two higher area velocity values. The oxidation value for the MHI catalyst at the lowest area velocity value appears to be erroneous, for the same reason as described above for the middle data point for the Prototech Pd #1. That is, the oxidation percentage at the lowest area velocity value should be higher, rather than lower than the value at the middle area velocity value.

Based on these results, it appears that the four catalysts to be tested at Monticello should include the Prototech gold, Carbon #6, Pd #1 from Supplier #2, and one of the two SCR catalysts. It would be difficult to clearly distinguish between the two SCR catalysts based on the data available, so this decision may be based on other factors, such as catalyst delivery and cost sharing.

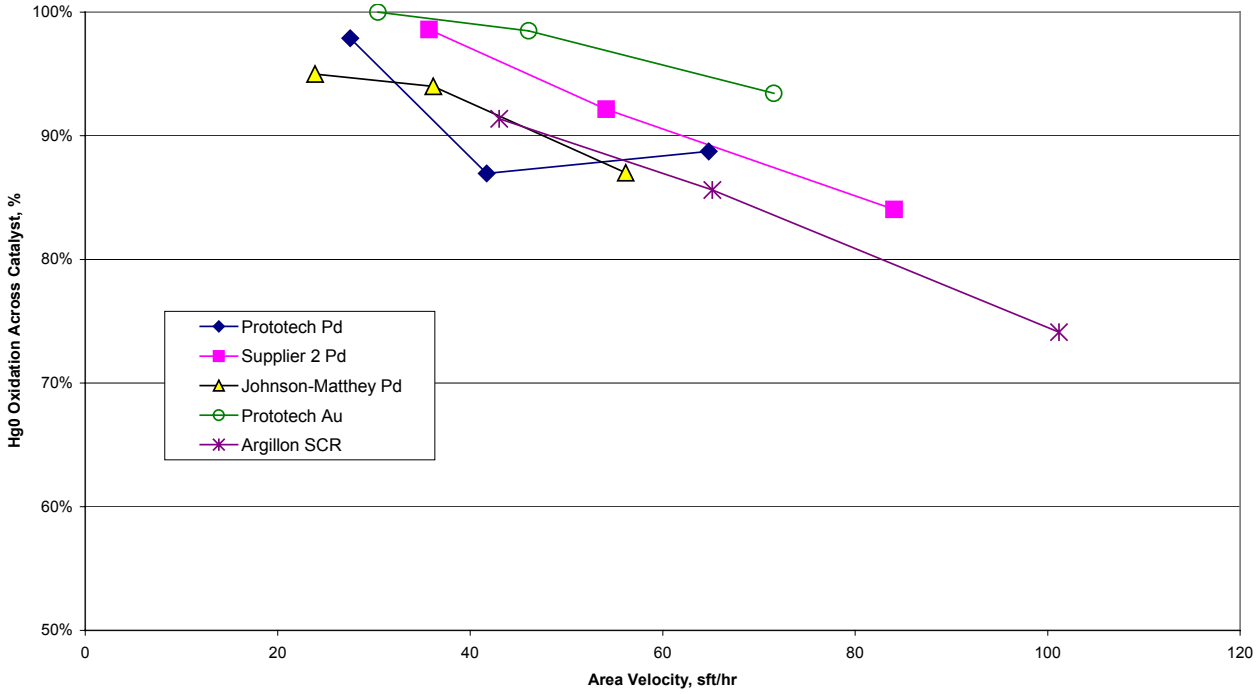

Figure 2. Catalyst Hg^0 Oxidation Activity Results from the Current Quarter at Simulated Monticello Plant Gas Conditions

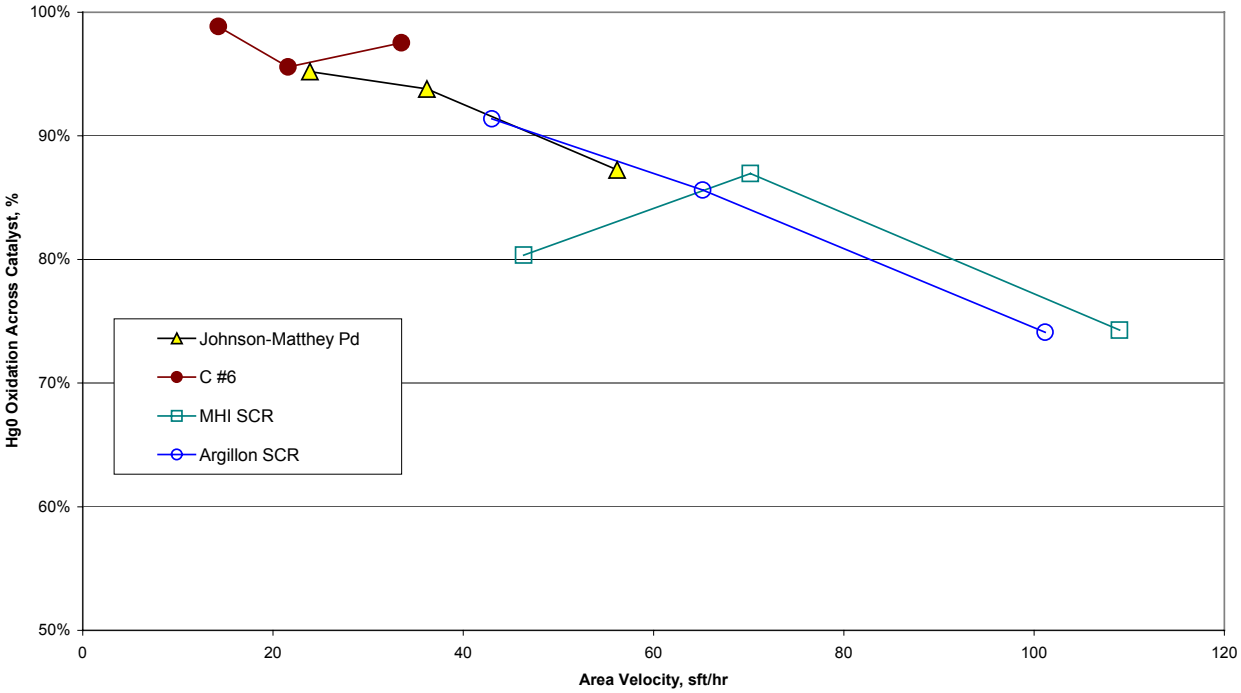

Figure 3. Catalyst Hg^0 Oxidation Activity from the Previous Quarter at Simulated Monticello Plant Gas Conditions

CONCLUSION

At this point in the project, only laboratory catalyst screening tests have been conducted; pilot-scale catalyst testing has not commenced. Based on the laboratory results to date, it appears that the four catalysts to be tested at Monticello should include the Prototech gold, Carbon #6, Pd #1 from Supplier #2, and one of the two SCR catalysts. It would be difficult to clearly distinguish between the two SCR catalysts based on the data available, so this decision may be based on other factors, such as catalyst delivery and cost sharing.

REFERENCES

1. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, October 1, 2002 – December 31, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. January 2003.

2. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, July 1, 2002 – September 30, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. October 2002.

3. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, March 1, 2002 – June 30, 2002. Cooperative Agreement No. DE-FC26-01NT41185, URS Corporation, Austin, Texas 78729. July 2002.

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5. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems, Final Report, Phase II,* U.S. Department of Energy Cooperative Agreement Number DE-AC22-95PC95260, URS Corporation, Austin, Texas 78729. June 2001.

6. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, January 1, 2004 – March 31, 2004. Cooperative Agreement No. DE-FC26-04NT41992, URS Corporation, Austin, Texas 78729. April 2004.